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Vapor−Liquid Equilibria of the 1-Butanol + *o*-Chlorophenol System. Effects of Association in the Vapor Phase

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Isothermal (at 363.15 and 383.15 K) and isobaric (at 20.00 and 50.00 kPa) vapor−liquid equilibria were obtained for the title system. On the basis of a heteroassociation in the vapor phase, the activity coefficients were found to be thermodynamically consistent and well-correlated with the Wilson equation.

Introduction

Vapor−liquid equilibrium (VLE) data are indispensable in the design of separation processes such as distillation columns and extractive distillation. These data are usually obtained from measurements, but also can be estimated from available predictive VLE models. In this sense, group-contribution methods such as UNIFAC (Fredenslund et al., 1977; Gmehling et al., 1982; Skjold-Jørgensen et al., 1979) have been shown to be a useful tool.

The group-contribution models require a complete and updated experimental VLE data bank in order to fit the group interaction parameters. In the last few decades, a great body of experimental data for mixtures of organic compounds has been reported. However, there is still a lack of experimental data, especially for some functional groups (Gmehling et al., 1993). One of the functional groups for which more experimental data are desirable is the phenol group (ACOH).

In this paper, isothermal (at 363.15 and 383.15 K) and isobaric (at 20.00 and 50.00 kPa) VLE data for the 1-butanol + *o*-chlorophenol system are presented. The vapor pressures of pure *o*-chlorophenol were also determined. These results allow the estimation of the interaction parameters between the functional groups ACOH and OH.

Experimental Section

Chemicals. 1-Butanol and *o*-chlorophenol (high purity grade, >99.9 and >99.0 mass %, respectively) from Aldrich Chemical were used without further purification. The purity of these chemicals was checked by gas chromatography (GLC). The physical properties of both compounds are listed in Table 1 along with literature values (Reid et al., 1977; Dean, 1985; Lide, 1990).

Apparatus and Procedure. The apparatus used in this work is an all-glass, dynamic recirculating still described by Walas (1985), equipped with a Cottrell pump. The still (Labodest model), manufactured by Fischer Labor und Verfahrenstechnik (Bonn, Germany) can handle pressures from 0.25 to 400 kPa and temperatures up to 523.15 K. In the boiler, with a volume of 80 cm^3, vapor bubbles are generated by external heating. The Cottrell pump ensures the intimate contact between the liquid and vapor phases and also with the sensing temperature elements. The equilibrium temperature is measured with a digital Fischer thermometer with an accuracy of ±0.1 K. For the pressure measurement, a digital manometer with an accuracy of ±0.01 kPa is used.

For the isobaric determinations, the pressure was fixed and the heating and shaking systems of the liquid mixture were turned on. For the isothermal experiments, the pressure was adjusted until the required temperature was achieved. In both cases, the system was kept at the boiling point for at least 30 min to ensure that the steady state was reached. At this moment, 0.2 cm^3 samples of liquid and condensed vapor of the Cottrell pump were taken with special syringes under partial vacuum.

Table 1. Physical Properties of Chemicals: Densities ϱ, Refractive Indexes n, and Boiling Points T_b

	ϱ(293.15 K)/(g·cm^{-3})		n(293.15 K)		T_b (50.00 kPa)/K	
compound	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.
1-butanol	0.809 50	0.8098	1.3988	1.3993	372.25	372.31[b]
o-chlorophenol	1.265 92	1.2634	1.5535	1.5524	421.85	421.95[c]

[a] Lide (1990). [b] Reid et al. (1977). [c] Dean (1985).

All the samples were analyzed with a Hewlett-Packard 5890 S-II gas chromatograph with a flame ionization detector. The GLC column was a 60 m, 0.2 mm i.d. fused silica capillary column, SUPELCOWAX 10. Chromatographic conditions were the following: oven temperature, 493.15 K; gas carrier, helium (30 cm^3·min^{-1}). The GLC response peaks were integrated with a Hewlett-Packard 3396 integrator.

The GLC was calibrated with gravimetrically prepared standard solutions. The standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made for each liquid and each vapor sample.

Results and Discussion

The experimental VLE results for the binary system at 363.15 and 383.15 K are given in Table 2. The isobaric data at 20.00 and 50.00 kPa are listed in Table 3.

To calculate the liquid-phase activity coefficients, γ_i, the Poynting factor was considered as unity at the experimental conditions. The fugacity coefficients were calculated on the basis of the virial equation of state, with the second virial coefficient being estimated by means of the Pitzer and Curl equations (1957) with the correction proposed by Tsonopoulos (1974). For every experimental pressure−temperature−composition condition, the calculated fugacity coefficients were close to unity, and were not considered in the analysis of the VLE data. So, the experimental liquid−phase activity coefficients γ_i were calculated from

$$\gamma_i = \frac{P y_i}{x_i P_i^\circ} \tag{1}$$

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Table 2. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Pressure P, and Activity Coefficients γ_i, for the 1-Butanol (1) + *o*-Chlorophenol (2) System at Constant Temperature T

T/K	x_1	y_1	P/kPa	γ_1	γ_2
363.15	0.000	0.000	6.43		
	0.032	0.121	6.99	0.779	0.987
	0.061	0.207	7.50	0.738	0.986
	0.102	0.334	8.20	0.780	0.946
	0.142	0.416	8.97	0.765	0.949
	0.196	0.531	9.87	0.782	0.894
	0.248	0.635	11.00	0.823	0.830
	0.265	0.657	11.27	0.815	0.818
	0.311	0.744	12.75	0.888	0.738
	0.389	0.785	14.41	0.849	0.789
	0.467	0.850	16.75	0.889	0.732
	0.545	0.911	19.29	0.941	0.586
	0.640	0.943	22.34	0.961	0.549
	0.733	0.966	25.45	0.979	0.509
	0.817	0.982	28.79	1.010	0.434
	0.892	0.991	31.50	1.021	0.408
	0.942	0.996	33.21	1.025	0.356
	1.000	1.000	34.22		
383.15	0.000	0.000	14.45		
	0.042	0.167	16.35	0.839	0.984
	0.077	0.272	17.63	0.803	0.962
	0.111	0.367	19.03	0.812	0.938
	0.150	0.440	20.76	0.786	0.947
	0.206	0.561	23.18	0.814	0.887
	0.275	0.674	26.19	0.828	0.815
	0.325	0.739	29.50	0.865	0.789
	0.416	0.827	33.47	0.858	0.686
	0.456	0.867	37.05	0.909	0.627
	0.517	0.897	41.42	0.927	0.611
	0.609	0.936	47.87	0.949	0.543
	0.668	0.955	52.12	0.962	0.485
	0.759	0.975	61.01	1.011	0.438
	0.815	0.983	65.70	1.022	0.418
	0.889	0.989	72.75	1.044	0.499
	0.927	0.993	76.27	1.054	0.506
	0.960	0.995	76.85	1.028	0.665
	1.000	1.000	77.52		

Vapor pressures P_i° were calculated with the Antoine equation

$$\ln(P_i^\circ/\mathrm{kPa}) = A - \frac{B}{(C + T/\mathrm{K})} \qquad (2)$$

For 1-butanol, the constants given in Reid et al. (1977) were used. The experimental vapor pressure data of pure *o*-chlorophenol are shown in Table 4. The constants in eq 2 (Table 4) were fitted by a nonlinear optimization method to minimize the mean relative deviation in P_i°. Experimental data were compared with literature values from Dean (1985) and Stephenson and Malanowski (1987), the mean relative deviations being 0.763% and 1.677%, respectively.

The thermodynamic consistency of the VLE experimental data was checked against the point-to-point test of Van Ness et al. (1973), modified by Fredenslund et al. (1977), using a four-parameter Legendre polynomial. The selected objective function to minimize was the sum of the squared relative deviations in the total pressure, SSRD(P):

$$\mathrm{SSRD}(P) = \sum\left(\frac{P_{\mathrm{exptl}} - P_{\mathrm{calcd}}}{P_{\mathrm{exptl}}}\right)^2 \qquad (3)$$

According with this test, the experimental data are consistent if the mean absolute deviation in y, MAD(y), is less than 0.01. As shown in Table 5, the data presented herein are not, with the assumptions considered, thermodynamically consistent.

Table 3. Vapor–Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature T, and Activity Coefficients γ_i, for the 1-Butanol (1) + *o*-Chlorophenol (2) System at Constant Pressure P

P/kPa	x_1	y_1	T/K	γ_1	γ_2
20.00	0.000	0.000	392.85		
	0.010	0.044	391.55	0.847	1.012
	0.026	0.108	390.05	0.844	1.012
	0.048	0.191	388.45	0.857	0.994
	0.063	0.233	387.75	0.817	0.982
	0.088	0.305	386.15	0.812	0.968
	0.116	0.361	384.35	0.779	0.981
	0.151	0.436	382.45	0.776	0.966
	0.206	0.546	379.55	0.796	0.927
	0.271	0.655	376.35	0.822	0.867
	0.332	0.723	373.35	0.835	0.854
	0.397	0.793	370.55	0.859	0.790
	0.475	0.848	367.25	0.881	0.762
	0.612	0.923	361.85	0.939	0.651
	0.711	0.971	358.35	0.992	0.389
	0.797	0.988	355.75	1.014	0.265
	0.829	0.988	354.55	1.030	0.326
	0.891	0.994	353.25	1.025	0.264
	0.928	0.996	352.35	1.029	0.278
	0.960	0.998	351.75	1.025	0.257
	1.000	1.000	351.35		
50.00	0.000	0.000	421.85		
	0.029	0.118	418.55	0.815	0.996
	0.065	0.242	415.55	0.808	0.974
	0.092	0.308	413.35	0.785	0.979
	0.151	0.468	408.05	0.856	0.949
	0.209	0.550	404.45	0.815	0.967
	0.244	0.614	402.25	0.841	0.931
	0.271	0.662	400.75	0.857	0.889
	0.326	0.716	397.95	0.845	0.888
	0.409	0.795	393.45	0.875	0.852
	0.498	0.866	389.05	0.916	0.763
	0.581	0.912	385.35	0.946	0.689
	0.634	0.935	383.45	0.955	0.627
	0.690	0.961	381.05	0.987	0.482
	0.765	0.978	378.25	1.010	0.402
	0.819	0.984	376.45	1.017	0.417
	0.860	0.989	375.35	1.019	0.360
	0.892	0.993	374.25	1.029	0.328
	0.936	0.995	372.85	1.040	0.408
	1.000	1.000	372.25		

Table 4. *o*-Chlorophenol Vapor Pressure P_i° Data as a Function of Temperature T and Antoine Constants

T/K	P_i°/kPa	T/K	P_i°/kPa	T/K	P_i°/kPa
337.05	1.91	390.55	18.40	427.85	59.97
348.35	3.29	393.35	20.42	431.05	65.45
353.85	4.29	395.65	22.05	433.85	70.69
358.35	5.25	398.65	24.33	436.85	76.48
362.65	6.30	401.15	26.42	439.45	81.99
369.15	8.25	403.85	28.85	440.95	85.11
374.85	10.28	410.05	35.00	442.85	89.15
379.55	12.32	416.05	42.40	444.85	93.66
383.35	14.16	419.95	47.90	445.85	96.50
387.25	16.32	424.55	54.60	447.65	101.14

	A	B	C
o-chlorophenol	14.061 22	3529.98	−73.896

Effects of Association in the Vapor Phase. In four sets of data, it was observed that by minimizing the mean deviation in total pressure in the thermodynamic consistency test, the calculated vapor compositions of 1-butanol were systematically smaller than the reported experimental values. If the vapor composition was adjusted, the calculated pressures were systematically greater than the experimental ones. Such deviations could be explained on the basis of an association in the vapor phase, in the way that some researchers have previously reported for mix-

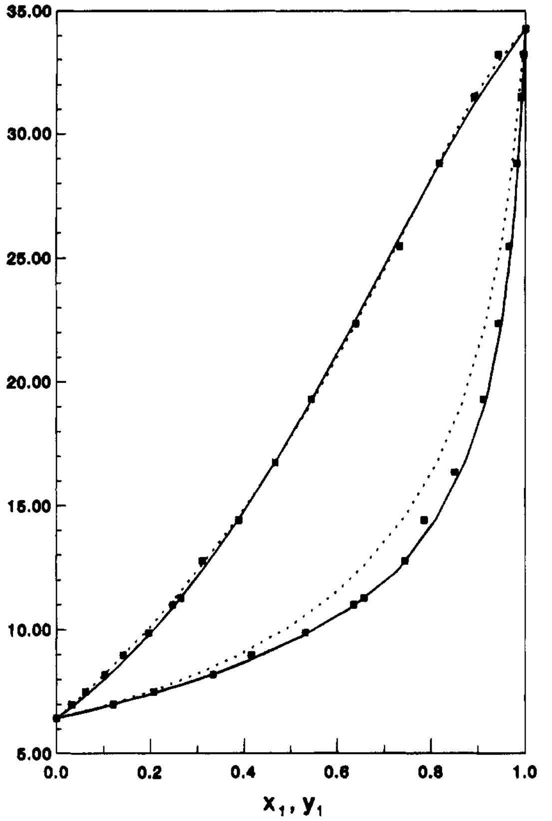

Figure 1. Pressure P vs composition (x_1, y_1) for the system 1-butanol (1) + *o*-chlorophenol (2) at constant temperature, T = 363.15 K: (■) experimental, (···) Wilson with no vapor correction, (—) Wilson with association in the vapor phase.

Table 5. Thermodynamic Consistency Test of the Experimental Data Assuming No Association and Association in the Vapor Phase: Mean Absolute Deviation MAD(*y*)

		MAD(*y*)	
		no association in vapor phase	association in vapor phase
T/K	363.15	0.0338	0.0077
	383.15	0.0337	0.0073
P/kPa	20.00	0.0214	0.0067
	50.00	0.0195	0.0083

tures of highly polar compounds (Wisniak and Tamir, 1975, 1988).

Since major deviations were observed for the intermediate liquid compositions, the data were tested assuming heterodimerization in the vapor phase. So, the following reversible reaction in the vapor phase was considered:

$$A_1 + A_2 \rightleftarrows A_{12};\quad K_{12}P = \frac{y'_{12}}{y'_1 y'_2} = \frac{\zeta(1-\zeta)}{(y_1-\zeta)(y_2-\zeta)} \qquad (4)$$

K_{12} being the equilibrium constant for the heterodimerization, P the total pressure, y'_1, y'_2, and y'_{12} the "true" mole fractions in the vapor phase for 1-butanol, *o*-chlorophenol, and the dimer, respectively, y_1 and y_2 the observed mole fractions in the vapor phase, and ζ the extent of reaction defined as

$$\zeta = \frac{n'_{12}}{n_1 + n_2} \qquad (5)$$

where n_i represents the number of moles of species i.

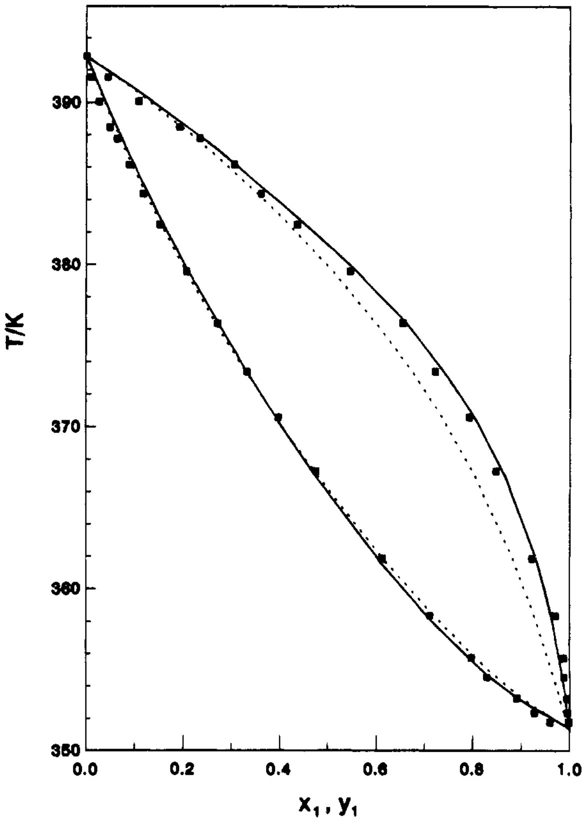

Figure 2. Temperature T vs composition (x_1, y_1) for the system 1-butanol (1) + *o*-chlorophenol (2) at constant pressure, P = 20.00 kPa: (■) experimental, (···) Wilson with no vapor correction, (—) Wilson with association in the vapor phase.

Table 6. Wilson Correlation Parameters for the Activity Coefficients and Mean Absolute Deviations MAD(*y*), MAD(*P*), and MAD(*T*)

		A_{12}/(J/mol)	A_{21}/(J/mol)	MAD(*y*)	MAD(*P*)/kPa	MAD(*T*)/K
T/K	363.15	−3171.98	6831.01	0.0086	0.18	
	383.15	−3611.38	9333.57	0.0030	0.75	
P/kPa	20.00	−3327.96	7998.86	0.0109		0.38
	50.00	−3378.58	7400.82	0.0079		0.27

In order to adjust the calculated pressure, the association effects are included by introducing correction factors for the partial pressure of both compounds. These factors were defined as

$$F_1 = \frac{y'_1}{y_1} \qquad F_2 = \frac{y'_2}{y_2} \qquad (6)$$

so that the total pressure was calculated as

$$P = x_1\gamma'_1 P_1^{\circ} F_1 + x_2\gamma'_2 P_2^{\circ} F_2 \qquad (7)$$

where γ'_1 and γ'_2 are the new activity coefficients to be fitted by nonideal VLE models.

To obtain the extent of reaction and thus the vapor true mole fractions, a correlation for K_{12} is needed. As not enough information about K_{12} is available, this constant was evaluated in the Wilson (Gmehling and Onken, 1977) fitting of the activity coefficients for the two isothermal sets of data. And, assuming a van't Hoff variation of K_{12} with the temperature, the expression for the dimerization constant is

$$\log(K_{12}/\text{kPa}^{-1}) = -10.129 + 3182/T/\text{K} \qquad (8)$$

The constants in eq 8 seem to be reasonable if compared with dimerization constants reported in the literature for carboxylic acids (Wisniak and Tamir, 1975), the slope being of the same order (3000−3300) and the K_{12} values 1−2 orders smaller.

Using eq 7 to represent the total pressure, the point-to-point thermodynamic consistency test was achieved, as shown in Table 5.

All the activity coefficients, γ'_1 and γ'_2, were correlated with the Wilson equation. The adjustable parameters A_{12} and A_{21} and the mean absolute deviations for the four systems are listed in Table 6. To fit the binary parameters, a nonlinear optimization method was used to minimize the mean absolute deviation in the total pressure, MAD(P).

The predicted results assuming association effects are according to the experimental values, while the model without association gave higher deviations. These effects are shown, for example, in Figures 1 and 2, for one isothermal and one isobaric set of data.

Conclusions

New VLE data for the 1-butanol + *o*-chlorophenol system are presented. The system shows negative deviations from ideality. In light of the results, association in the vapor phase must be considered in order to predict the VLE experimental behavior. Using the expression obtained from the isothermal data for the heterodimerization equilibrium constant, the isobaric data were tested, and good agreement was reached. Although the simplest model of association was selected, the predictions were highly improved.

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